RESEARCH ARTICLE

Structural and Dielectric Response of SnO_2 / $ZnSnO_3$ Nanostructures

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ABSTRACT: Large-scale novel $SnO_2/ZnSnO_3$ microspheres were successfully synthesized by a simple hydrothermal method with with the interaction of UV radiation. The polarization mechanism in accordance with an applied electric field was examined. Important dielectric parameters like dielectric constant, dielectric loss and ac conductivity are discussedthe help of the surfactant urea. The as-synthesized samples were characterized using X-ray powder diffraction (XRD), scanning electron microscopy (SEM), UV visible spectroscopy and Dielectric techniques. XRD and SEM results revealed the existence of a mixture of $SnO_2/ZnSnO_3$ phases. The electronic band structure is analyzed.

KEYWORDS: Zinc Stannate, Hydrothermal, Urea, SEM, Dielectric

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I. INTRODUCTION

Direct synthesis of nano- or micro sized material with controlled shape and morphology has attracted considerable interest, because it is well-known that the properties of material depend not only on their composition, but also on their structure, phase, shape and size [1–4]. Functional materials with novel morphology can be used to exploit new potential applications. To fabricate the complex architectures based on one dimensional nano structures, various strategies have been employed successfully to assemble building blocks into different morphology. However, these approaches usually involve costly templates or raw materials and complex operating steps, which possibly result in the increased cost and further limit the potential applications. Therefore, the development of a novel, facile, and low cost route to synthesis nanostructure materials, control of their shapes, and exploration underlying growth mechanisms are very important issues for understanding relationships between the materials morphologies/structures and their properties and smart assembling of nanomaterials toward their effective applications.

Tin oxide (SnO2) and zinc stannate (ZnSnO3), as famous multifunctional materials, have recently attracted considerable attention due to interesting technological properties and potential applications in various fields such as gas sensors, moisture detectors, and electronics materials [5-8]. It is well-known that the size and morphology of such materials very strongly affect their properties and applications [3,9]. Recently, several methods have been employed to prepare SnO_2 and $ZnSnO_3$ nano- and microstructures, including template-directed, vapor–liquid–solid (VLS), chemical–vapor-deposition (CVD), thermal evaporation, and solution-phase chemical methods. [8,10,11] Of these techniques, hydrothermal method is one of the most promising routes, due to its low cost and potential advantage for large-scale production.[12].

In this work, we focus the structural and morphological analysis of $SnO_2/ZnSnO_3$ nanoparticles prepared by hydrothermal method and the energy band structure is studied by the UV interaction. Complete dielectric important parameters are too exemplified.

II.PREPARATION

All chemicals were used without any further purification. The preparation of $ZnSnO_3/SnO_2$ is based on the following reaction:

$$2SnCl_4 5H_2O + Zn(CH_3COO)_2.2H_2O + 6NaOH \longrightarrow ZnSnO_3 + SnO_2 + 4NaCl_2 + 2Na(CH_3COO)_2 + 3H_2O$$

The tin chloride penta hydrate ($SnCl_4.5H_2O$, analytical grade) and zinc acetate dehydrate ($Zn(CH_3COO)_2.2H_2O$, analytical grade) were used as main precursors materials. A solution of 30ml of ethlediamine added with 30 ml of double distilled water is prepared. 0.16M of Tin chloride penta hydrate is added into this mixture, with this mixture approximately of about 0.08M of zinc which is in the form of zinc acetate dihydrate compound is added to the mixture and allowed to stir and well mixed solution is added with exactly 0.8M of urea. After the addition of urea, then NaOH of about 0.96 g (0.8M) is added this mixture is transferred to autoclave, maintained at 180^0c for 12 hours and allowed to cool to the room temperature then centrifuge process with double distilled water and ethanol and dried for 15 hours at 90^0c. Finally we obtained a 2:1nano composite of SnO_2 & $ZnSnO_3$.

3. RESULTS AND DISCUSSION.

3.1. XRD analysis

The XRD pattern of the product is shown in Figure 1. The peaks at 2θ values of 26.3°, 51.4°, 65.6° and 71.2° can be associated with (1 1 0), (2 1 1), (3 0 1) and (2 0 2) respectively. A matching of the observed and standard (hkl) planes confirmed that Product is of SnO_2 having a tetragonal structure. Then, the peaks at 2θ values of 26.3°, 33.7°, 58.0^0 and 60.2° can be associated with (1 1 0), (1 0 1) and (0 0 2) respectively. A matching of the observed and standard (hkl)

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Received: 25.06.2016 **Accepted:** 12.07.2016 **Published on**: 22.07.2016

planes confirmed the appearance of $ZnSnO_3$.The average crystallite

size (D) was estimated using the Scherer equation as follows,

$$D = \frac{K\lambda}{\beta COS\theta}$$

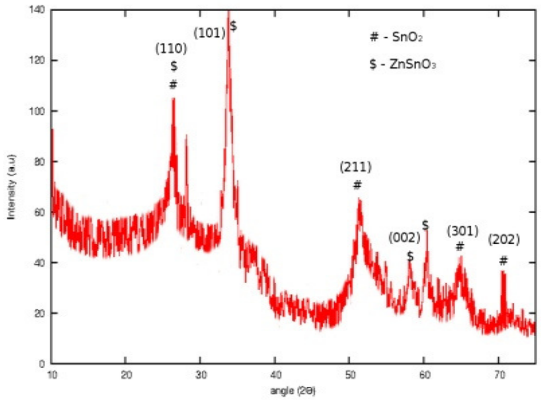

Fig 1 XRD pattern of the sample $SnO_2/ZnSnO_3$

3.2. Morphological analysis

Scanning Electron Microscopy (SEM) is a vital characterization tool for directly imaging nanomaterials to obtain quantitative measures of grain size, size distribution, and morphology.

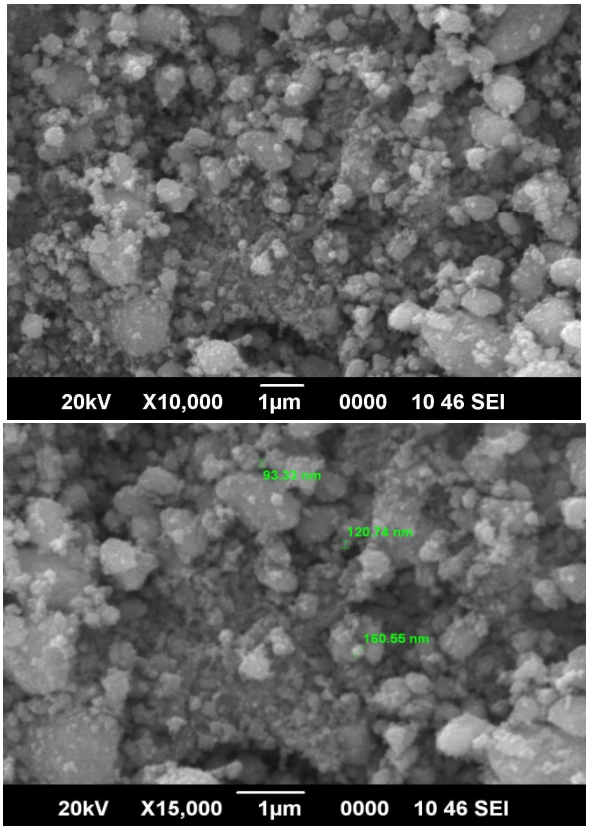

Figure 2 shows the unique morphology of the as-synthesized $SnO_2/ZnSnO_3$ hollow nanospheres SEM Micrographs at 1 μm offer better outstanding about passivation of $SnO_2/ZnSnO_3$ nanocomposite growth aspect. Images showed the developed shape of the composite and exhibit uniform particles with diameter of 90-150 nm. Further a close examination of figure shows the absence of agglomeration to a large extent in the particles synthesized via hydrothermal method.

3. 3. UV Studies

The optical reflectance of $SnO_2/ZnSnO_3$ as-synthesized composite is done using VARIAN CARY 5000 spectrophotometer in the range of 200 to 900 nm and is shown in Figure 3. The spectra show large reflectance window between 400 nm and 800 nm and has a sharp absorption edge at about 303 nm The cut-off behavior at the blue end of the spectrum is determined by direct electronic transitions from valance band to the conduction band. The combined effect of SnO_2 and $ZnSnO_3$ materials are exemplified in the presented spectrum. The absorption edge of $SnO_2/ZnSnO_3$ nano composite has shift towards lower wavelengths. By combining the reflection with sample thickness we were able to calculate absorption co-efficient and thus band gap. The calculated E_g value is 4.1 eV. This showed that optical band gap widening occurs due to the reduction in particles' size and also as a result of change of the low content SnO_2 particle interaction energy, which is depending on the ionization energy of the dopant impurity.

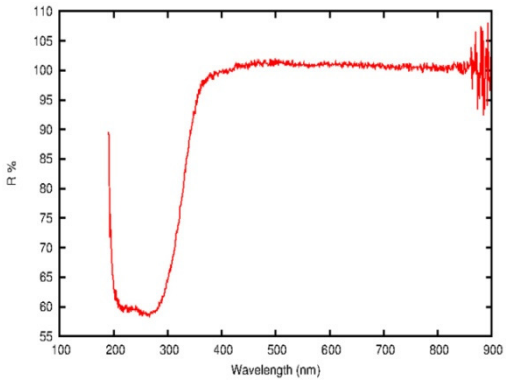

Fig. 3 UV Studies of $SnO_2/ZnSnO_3$

3.4. Dielectric measurements

The dielectric measurements have been carried out using capacitive-arrangement technique with the help of LCR impedance analyzer. In the following section, we are discussing the dielectric parameters like dielectric constant, dielectric loss and alternating current conductivity. We investigated the variation of dielectric parameters by varying frequency from 50 Hz to 1 MHz The dielectric constant of the sample is calculated using the relation ε_r = C d / ε_0A; where the $SnO_2/ZnSnO_3$pellete acts as a dielectric with the □0 absolute permittivity, C is the capacitance, d is the thickness and A is the area. It is seen from the figure 4 that the prepared composite's relative permittivity is higher at lower frequencies and decreases with increase in frequency..Its value is almost unchangeable at higher electromagnetic frequency region. The decrement in the value is shown in the frequency window of 50 Hz to 1 kHz and it remains almost constant while we are moving to higher frequencies. The value of dielectric constant is 88.8 at 100 Hz and it reduces up to 23 at 1 kHz frequency region. From the literature it is learnt that Zn substitution has

increased the dielectric constant. In our case also same trend is observed.

Figure 5 shows the variation of dielectric loss of $SnO_2/ZnSnO_3$nanocomposite as a function of frequency. The term, dielectric loss, is associated with the energy loss while the electric field passes through the sample. The trend in the variations of both dielectric constant and dielectric loss as a function of frequency is the same. The higher value for both dielectric constant and loss are attributed to polarization mechanism. It is well known that there are two major dielectric polarization, that is rotation direction polarization (RDP) process and space charge polarization (SCP) process that contribute to the enhanced dielectric behavior of nanomaterials. We suggest that both RDP and SCP process contribute to the enhancement of dielectric response of the $SnO_2/ZnSnO_3$nanocomposite. Dielectric loss shows larger values in the lower frequency region is due to the loss associated with dipolar movement and Zn substitution in the nano composites. Moving to higher frequencies, dipoles cannot align in accordance with electric flux reversals so that less energy loss.

The a. c. conductivity of $SnO_2/ZnSnO_3$ nano structure is calculated with the data available from dielectric measurement and by using the relation: $\sigma_{ac}= 2 \pi f \varepsilon_0 \varepsilon_r \tan\delta$ Where, f is the frequency of applied field, tan δ is loss tangent (ratio of imaginary part of dielectric permittivity to real part of dielectric permittivity) available from dielectric measurement, ε_r is the relative permittivity of the sample and ε_0 is the dielectric permittivity of vacuum (8.854×10^{-12} F/m). The alternating current conductivity is directly proportional to frequency and is well examined with figure 6.

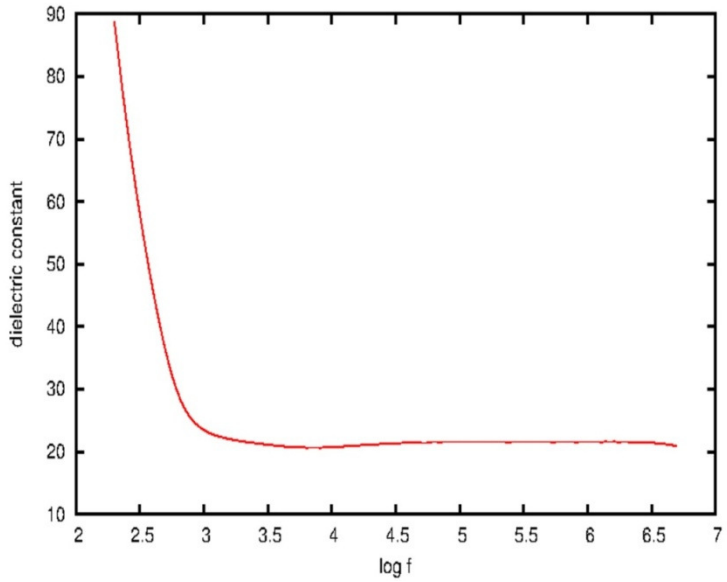

Figure 4: The variation of dielectric constant of $SnO_2/ZnSnO_3$composite in accordance with frequency

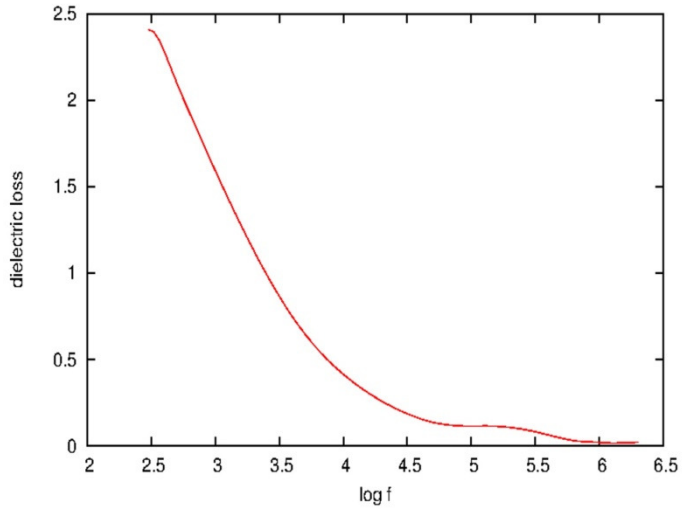

Figure 5: Frequency dependent dielectric loss of $SnO_2/ZnSnO_3$ composite

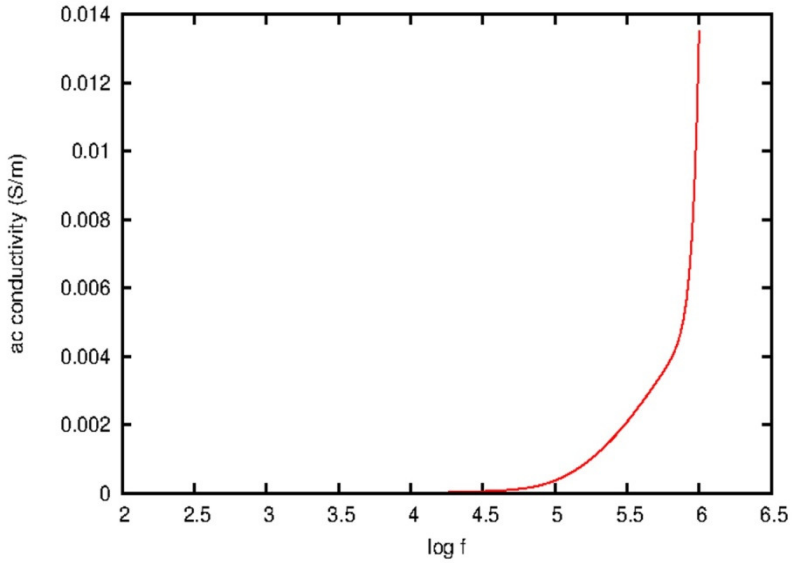

Figure 6: Variation of ac conductivity with electric field frequency of $SnO_2/ZnSnO_3$ composite

4. CONCLUSION.

A simple preparation method for $SnO_2/ZnSnO_3$ composite could be established. The structural and morphological analysis was done using X-ray diffraction spectroscopy and SEM micrographs. In XRD spectrum, the intensity peaks of as-synthesized composite were attributed to SnO_2 and $ZnSnO_3$ individually. The SEM images showed the developed shape of the composite and exhibit uniform particles with diameter of 90-150 nm. UV spectrum analysis exemplified the sample's absorption edge and the calculated band gap is 4.1 eV. Important dielectric parameters such as dielectric constant and dielectric loss were determined and the low frequency dielectric relaxation mechanism was discussed in detail. Composite possessed high ac conductivity values at higher frequency region.

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